

THE CONFIGURATIONAL STABILITY OF OXIME ANIONS

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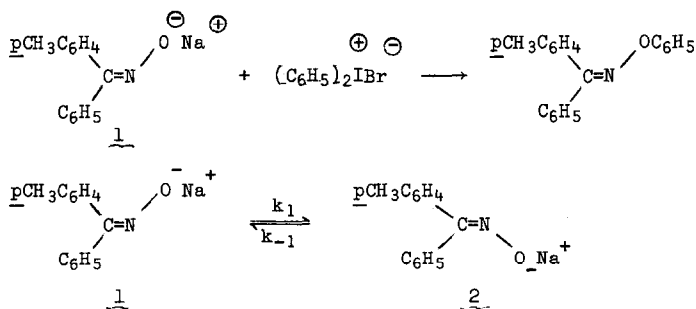
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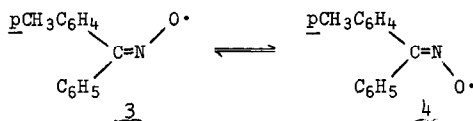
Numerous investigations of geometric isomerizations of imine derivatives have been reported in recent years (1). Interest in these systems derives, in part, from the remarkable sensitivity of syn-anti isomerization rates to structural changes. For example, among imino compounds derived from benzophenone, changes in groups attached to nitrogen produce a range of rates of uncatalyzed isomerizations of greater than 14 powers of 10 (2,3). Attempts to elucidate the mechanisms (lateral shift, rotational, or intermediate possibilities) of individual isomerizations continue to challenge the ingenuity of various research groups and provide fuel for controversy.

The great thermal configurational stability of O-alkyl oximes has been reported (2) and several kinetic studies of the syn-anti isomerizations of oximes have appeared (4,5). Surprisingly, almost no kinetic data for comparable isomerizations of oxime anions are available (6). Numerous references in the literature related to alkylations and arylations of oxime anions suggest that these anions possess at least modest configurational stability (8). And a number of other qualitative observations bearing on the geometrical isomerizations of oxime anions have been reported (9).

Our experience (10) with the stereospecific phenylation of Z-sodium 4-methylbenzophenone oximate (1) led us to study the rates of interconversion of 1 and its geometric isomer 2. A



concurrent investigation of the rates of interconversion of the corresponding diaryl iminoxy radicals 3 and 4 made a comparison of the kinetics of these two related isomerizations attractive (11).



Configurational assignments for the two parent oximes (conjugate acids of 1 and 2) have already been described (12). The isomerization rates were conveniently determined by nmr by following the changes in intensities of the two methyl proton singlets, the chemical shifts for which differ by approximately 0.07 ppm. Isomerically pure samples of the oximes in absolute methanol were converted to the anions with an excess of sodium methoxide. The solutions (approximately 0.09 M in oxime anion) were degassed and the isomerization rates determined as mentioned above. The first-order rate constant,  $k_1$ , at  $144^\circ$  was found to be  $3.1 \pm 0.2 \times 10^{-5} \text{ sec}^{-1}$ . The equilibrium constant under these conditions is 1.6. The rates were also determined at  $135^\circ$  and  $160^\circ$  leading to the activation parameters  $E_a = 26 \pm 2 \text{ Kcal/mole}$  and  $\Delta S^\ddagger = -20 \pm 7 \text{ eu}$ . An extrapolation of the rate constant,  $k_1$ , to  $60^\circ$  places this syn-anti isomerization rate within the range of those for N-halo benzophenone imine derivatives (2). Thus among diarylketimine derivatives only O-alkyl oximes have appreciably greater configurational stability (2).

A number of theoretical studies bearing upon the mechanisms of syn-anti isomerizations of imine derivatives have been reported. Lehn and co-workers have presented ab initio SCF-LCAO-MO calculations comparing energy barriers for inversion and rotation in methylenimine (13). The rotational energy barrier was computed to be considerably higher than the "in plane" inversion barrier. Similar results for methylenimine were obtained by Raban employing CNDO/2 semi-empirical SCF-MO methods (14). Effects of heteroatoms attached to carbon were also explored (see Table 1).

We have performed calculations for the acetone oxime anion system using both extended Hückel and CNDO/2 methods. The assumed geometry is as indicated in Figure 1. The two methyl carbons

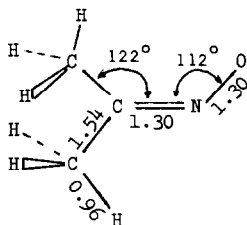


Figure 1. ASSUMED GEOMETRIC PARAMETERS FOR THE ACETONE OXIME ANION

were assumed to have tetrahedral geometry. Ground state calculations were made for this geometry, for a linear C-N-O structure (lateral shift transition state), and for a geometry in which the oxygen has been rotated about the C-N bond through a 90° dihedral angle (rotational transition state) (15). The results, along with comparison calculations of Lehn and of Raban are listed in Table 1.

Table 1. ISOMERIZATION BARRIERS CALCULATED FOR SEVERAL IMINE DERIVATIVES

Isomerization Type	CH <sub>2</sub> =NH <sup>a</sup>	CH <sub>2</sub> =NH <sup>b</sup>	HOCH=NH <sup>b</sup>	(NH <sub>2</sub> ) <sub>2</sub> C=NH <sup>b</sup>	(CH <sub>3</sub> ) <sub>2</sub> C=NO <sup>⊖</sup> <sup>c</sup>	
					CNDO/2	Ext. Hückel
Inversion	26-28	31.1	31.8	36.1	28	18
Rotation	57	61.1	50.7	28.4	106	25

(a) Lehn (ab initio); (b) Raban (CNDO/2); (c) Present study

The unusually close agreement between our calculated (CNDO/2) barrier to a linear inversion for the acetoxime anion and the experimentally determined E<sub>a</sub> for the 4-methylbenzophenone oxime anion is, no doubt, fortuitous. In this respect the calculations for this mode of isomerization could be reasonably anticipated from the calculations of others. However, the results do suggest that an out of plane rotational mechanism for the oxime anion isomerization is unlikely.

The estimated rotational barrier for the acetoxime anion is, in contrast, much higher than similar rotational barriers in imines (16). This CNDO/2 calculation may well exaggerate the rotational barrier. Nonetheless, our calculations suggest that in order to rotate oxygen about the C-N bond axis, in addition to reducing C-N bonding, the N=C=O bond order, both π and σ, must be reduced. In the other imine cases, this type of "bond reduction effect" is absent in the N-H bond, so rotational barriers might be expected to be lower. We are making further calculations to determine optimum geometries for the C-N-O group and to study the energy profile as the group "inverts" or "rotates."

We have recently shown that the rates of geometric isomerization of iminoxy radicals are 5 to 6 orders of magnitude larger than those of corresponding oxime anions (11). This comparison has been discussed elsewhere (11).

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15. The bond-lengths were not optimized for minimum energy and were held constant in all configurations. Thus barriers can be considered only rough approximations.
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